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Rapid Method for Sodium Hydroxide Fusion of Limestone Matrices Prior to Americium, Plutonium, Strontium, Radium, and Uranium Analyses for Environmental Remediation Following Radiological Incidents

U.S. Environmental Protection Agency

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Sodium Hydroxide Fusion of Limestone Matrices

Revision History

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Rapid Method for Sodium Hydroxide Fusion of Limestone Matrices Prior to Americium, Plutonium, Strontium, Radium, and Uranium Analyses

1. Scope and Application

- 1.1. This method is applicable to the sodium hydroxide fusion of limestone samples, prior to chemical separation as described in the following procedures:
 - 1.1.1. Rapid Radiochemical Method for Americium-241 in Building Materials for Environmental Remediation Following Radiological Incidents (Reference 16.1).
 - 1.1.2. Rapid Radiochemical Method for Plutonium-238 and Plutonium-239/240 in Building Materials for Environmental Remediation Following Radiological Incidents (Reference 16.2).
 - 1.1.3. Improved Rapid Radiochemical Method for Radium-226 in Building Materials for Environmental Remediation Following Radiological Incidents (Reference 16.3).
 - 1.1.4. Rapid Radiochemical Method for Total Radiostrontium (Sr-90) in Building Materials for Environmental Remediation Following Radiological Incidents (Reference 16.4).
 - 1.1.5. Rapid Radiochemical Method for Isotopic Uranium in Building Materials for Environmental Remediation Following Radiological Incidents (Reference 16.5).
- 1.2. This is a general method for limestone samples collected following a radiological or nuclear incident. The limestone samples may be received as core samples, crushed samples, or in pieces of various sizes.
- 1.3. The rapid fusion method is rapid and rigorous, effectively digesting refractory radionuclide particles that may be present in the limestone samples.
- 1.4. Limestone samples should be crushed and pulverized prior to taking a representative aliquant for analysis. The limestone sample should be milled to achieve a particle size small enough that representative subsamples can be taken and representative aliquants analyzed.
- 1.5. After a homogeneous subsample is obtained, the limestone sample aliquant is taken and fused to digest the limestone sample matrix, and matrix removal steps are employed to collect and preconcentrate the radionuclides from the alkaline fusion matrix. This method is a sample digestion and pretreatment technique to be used prior to other separation and analysis methods. The user should refer to those individual methods and any project-specific requirements for the determination of applicable measurement quality objectives (MQOs).

Note: Sample count times may vary based on differences in instrument parameters such as chemical yield, detection efficiency, and background.

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1.6. Application of this method by any laboratory should be validated by the laboratory using the protocols provided in *Method Validation Guide for Qualifying Methods Used by Radioanalytical Laboratories Participating in Incident Response Activities* (Reference 16.6), or the protocols published by a recognized standards organization for method validation.

1.6.1. In the absence of project-specific guidance, MQOs for limestone samples may be based on the analytical action levels (AALs), required method uncertainty (u_{mr}), and the required relative method uncertainty (ϕ_{mr}) found in the *Radiological Sample Analysis Guide for Incident Response — Radionuclides in Soil* (Reference 16.7).

2. Summary of Method

- 2.1. The method is based on the rapid dissolution of a representative, finely milled aliquants of approximately 1 g of limestone using sodium hydroxide fusion at 600 °C.
- 2.2. Plutonium (Pu), Uranium (U), and Americium (Am) are separated from the alkaline matrix using an iron hydroxide/titanium hydroxide precipitation followed by a lanthanum fluoride matrix removal step.
- 2.3. Strontium (Sr) is separated from the alkaline matrix using a phosphate precipitation, followed by a calcium fluoride precipitation to remove silicates.
- 2.4. Radium (Ra) is separated from the alkaline matrix using a carbonate precipitation.
- 2.5. The resulting solutions are subsequently processed as summarized in Steps 1.1.1–1.1.5.

3. Definitions, Abbreviations and Acronyms

- 3.1. Discrete Radioactive Particles (DRPs or “hot particles”). Particulate matter in a sample of any matrix where a high concentration of radioactive material is present as a tiny particle (μm [micron] range).
- 3.2. *Multi-Agency Radiological Analytical Laboratory Protocol (MARLAP) Manual* (Reference 16.8).
- 3.3. The use of the term limestone throughout this method is not intended to be limiting or prescriptive, and the method described herein refers to all limestone- related materials. In cases where the distinction is important, the specific issues related to a particular sample type will be discussed.

4. Interferences and Limitations

- 4.1. Limestone samples with larger particle size may require a longer fusion time during Step 11.1.7.
- 4.2. Information regarding the elemental composition of the sample may be helpful. For example, limestone may have native concentrations of uranium, radium, thorium (Th), strontium, or barium (Ba), any of which may have an effect on the chemical

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separations used following the fusion of the sample. In some cases (e.g., strontium analysis), elemental analysis of the digestate prior to chemical separations may be necessary to determine native concentrations of carrier elements present in the sample. The amount of stable Sr added to the limestone samples is designed to minimize the impact from native stable strontium.

- 4.3. Matrix blanks for these matrices may not be practical to obtain. Efforts should be made to obtain independent, analyte-free materials that have similar composition as the samples to be analyzed. These blanks will serve as process monitors for the fusion process, and as potential monitors for cross contamination during batch processing.
- 4.4. Uncontaminated limestone material may be acceptable blank material for Pu, Am, and Sr analyses, but this material will contain background levels of naturally occurring U and Ra isotopes.
 - 4.4.1. If analyte-free blank material is not available and an empty crucible is used to generate a reagent blank sample, it is recommended that ~200 milligram (mg) calcium be added as calcium nitrate to the empty crucible as blank simulant for limestone. This simulates the calcium present in the limestone sample, which is utilized in the sample preconcentration steps.
 - 4.4.2. Tracer yields may be slightly lower for reagent blank matrices, since limestone matrix components typically enhance recoveries across the precipitation steps.
- 4.5. Samples with elevated activity or samples that require multiple analyses from a single aliquant may need to be split after dissolution. In these cases the initial digestate and the split fractions should be carefully measured to ensure that the sample aliquant for analysis is accurately determined.
 - 4.5.1. Tracer or carrier amounts (added for yield determination) may be increased where the split allows for the normal added amount to be present in the subsequent aliquant. For very high activity samples, the addition of the tracer or carrier may need to be postponed until following the split, in which case special care must be taken to ensure that the process is quantitative until isotopic exchange with the yield monitor is achieved. This deviation from the method should be thoroughly documented and reported in the case narrative.
 - 4.5.2. When this method is employed and the entire volume of fused sample is processed in the subsequent chemical separation method, the original sample size and units are used in all calculations, with the final results reported in the units requested by the project manager.
 - 4.5.3. In cases where the sample digestate is split prior to analysis, the fractional aliquant of the sample is used to determine the sample size. The calculation of the appropriate sample size used for analysis is described in Section 12.
- 4.6. Batch blank samples, laboratory control samples (LCS), and duplicates should be created as early in the process as possible, following the same tracer/carrier additions, digestion process, and sample splitting used for the field samples. In this method, quality control (QC) samples should be initiated at the point samples are aliquanted into crucibles for the fusion.

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- 4.7. Zirconium crucibles used in the fusion process may be reused.
 - 4.7.1. Before reuse, the crucibles should be cleaned very well using soap and water, followed by warm nitric acid (multiple rinses) and then water. Blank measurements should be monitored to ensure effective cleaning and control against cross-contamination.
 - 4.7.2. Segregation of crucibles into separate groups used for low and high activity samples is recommended to minimize the risk of cross-contamination while maximizing the efficient use of crucibles.
- 4.8. Centrifuge speeds of 3500 revolutions per minute (rpm) are recommended but lower rpm speeds may be used if 3500 rpm is not available. Longer centrifuge times may be needed with lower speeds.
- 4.9. Aluminum nitrate reagent typically contains trace levels of uranium contamination. To achieve the lowest possible blanks for isotopic uranium measurements, some labs have removed the trace uranium by passing ~250 milliliter (mL) of the 2 Molar (M) aluminum nitrate reagent through ~7 mL TRU Resin, but this will have to be tested and validated by the laboratory.
- 4.10. The high calcium (Ca) content in limestone may limit the sample size used for the determinations of some radionuclides, particularly for ^{226}Ra analyses where a calcium carbonate preconcentration step is used and high levels of calcium (Ca) could exceed resin capacity. The sample aliquant is limited to 0.75 g, and additional cation resin is prescribed to address this.
- 4.11. Because of the high calcium content in limestone, the native amounts of calcium in the sample aliquants are utilized during many of the preconcentration steps, such as the calcium carbonate, calcium phosphate, or calcium fluoride precipitation steps. Additional calcium is not added during these steps to avoid problems associated with having too much calcium, such as undissolved solids in the final column load solutions. By adding calcium to the reagent blank and laboratory control sample (LCS) crucibles to simulate the limestone samples, the blank and LCS behave like the sample.
- 4.12. A 1-g aliquant is used for the actinide analysis. For the actinide co-precipitation step, the hydroxide content is reduced by adding acid to the fusion matrix to reduce Ca in the iron hydroxide precipitate. This reduces the size of the calcium fluoride/lanthanum fluoride ($\text{CaF}_2/\text{LaF}_3$) precipitate so that it can be dissolved effectively into the column load solution for processing.

5. Safety

5.1. General

- 5.1.1. Refer to your laboratory's safety manual for concerns of contamination control, personal exposure monitoring and radiation dose monitoring.
- 5.1.2. Refer to your laboratory's chemical hygiene plan (or equivalent) for general safety rules regarding chemicals in the workplace.

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5.2. Radiological

5.2.1. Discrete Radioactive Particles (DRPs or “hot particles”)

5.2.1.1. Hot particles will likely be small, on the order of 1 millimeter (mm) or less. DRPs typically are not evenly distributed in the media and their radiation emissions are not uniform in all directions (anisotropic).

5.2.1.2. Limestone media should be individually surveyed using a thickness of the solid sample that is appropriate for detection of the radionuclide decay particles.

NOTE: The information regarding DRPs should accompany the samples during processing as well as be described in the case narrative that accompanies the sample results.

5.3. Procedure-Specific Non-Radiological Hazards:

5.3.1. The sodium hydroxide fusion is performed in a furnace at 600 °C. The operator should exercise extreme care when using the furnace and when handling the hot crucibles. Long tongs are recommended. Thermal protection gloves are also recommended when performing this part of the procedure. The fusion furnace should be used in a well-ventilated area (hood, trunk exhaust, etc.).

5.3.2. Particular attention should be paid to the use of hydrofluoric acid (HF). Hydrofluoric acid is an extremely dangerous chemical used in the preparation of some of the reagents and in the microprecipitation procedure. Appropriate personal protective equipment (PPE) must be used in strict accordance with the laboratory safety program specification.

6. Equipment and Supplies

6.1. Adjustable temperature laboratory hotplates.

6.2. Balance, top loading or analytical, readout display of at least ± 0.01 g.

6.3. Beakers, 100 mL and 150 mL capacity.

6.4. Centrifuge able to accommodate 225 mL (or 250 mL) tubes.

6.5. Centrifuge tubes, 50 mL and 225 mL capacity.

NOTE: 225-mL centrifuge tubes are specified but 250 mL centrifuge tubes may also be used instead.

6.6. Crucibles, 250 mL, zirconium, with lids.

6.7. 100 microliters (μL), 200 μL , 500 μL , and 1 mL pipets or equivalent and appropriate plastic tips.

6.8. 1–10 mL electronic/manual pipet(s).

6.9. Hot water bath or dry bath equivalent.

6.10. Muffle furnace capable of reaching at least 600 °C.

6.11. Tongs for handling crucibles (small and long tongs).

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- 6.12. Tweezers or forceps.
- 6.13. Sample size reduction equipment (hydraulic press, milling equipment, mallet, etc.) and screens. The necessary equipment will be based on a laboratory's specific method for the process of producing a uniformly ground sample from which to procure an aliquant.

NOTE: See Appendix A for a method for homogenization of limestone samples.

- 6.14. Vortex stirrer.

7. Reagents and Standards

NOTES: Unless otherwise indicated, all references to water should be understood to mean Type I reagent water (ASTM D1193; Reference 16.9).

All reagents are American Chemical Society (ACS)-grade or equivalent unless otherwise specified.

- 7.1. Type I reagent water as defined in ASTM Standard D1193 (Reference 16.9).
- 7.2. Aluminum nitrate solution, 2M ($\text{Al}(\text{NO}_3)_3$): Add 750 g of aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) to ~700 mL of water and dilute with water to 1 liter (L).
- 7.3. Ammonium hydrogen phosphate (3.2M): Dissolve 106 g of $(\text{NH}_4)_2\text{HPO}_4$ in 200 mL of water, heat on low to medium heat on a hot plate to dissolve and dilute with water to 250 mL.
- 7.4. Boric Acid, H_3BO_3 .
- 7.5. Calcium nitrate (1.25M): Dissolve 147 g of calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) in 300 mL of water and dilute with water to 500 mL.
- 7.6. Iron (Fe) carrier (50 mg/mL): Dissolve 181 g of ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in 300 mL water and dilute with water to 500 mL. This carrier does not need to be standardized.
- 7.7. Hydrochloric acid (12M): Concentrated HCl.
 - 7.7.1. Hydrochloric acid (0.01M): Add 0.83 mL of concentrated HCl to 800 mL of water and dilute with water to 1 L.
 - 7.7.2. Hydrochloric acid (1.5M): Add 125 mL of concentrated HCl to 800 mL of water and dilute with water to 1 L.
- 7.8. Hydrofluoric acid (28M): Concentrated HF.
- 7.9. Lanthanum (La) carrier (1.0 mg La^{3+} /mL): Add 1.56 g lanthanum (III) nitrate hexahydrate [$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$] in 300 mL water, dilute with water to 500 mL. This carrier does not need to be standardized.
- 7.10. Nitric acid (16M): Concentrated HNO_3 .
 - 7.10.1. Nitric acid (3M): Add 191 mL of concentrated HNO_3 to 700 mL of water and dilute with water to 1 L.

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- 7.10.2. Nitric acid (3M)–boric acid (0.25M) solution: Add 15.4 g of boric acid and 190 mL of concentrated HNO₃ to 500 mL of water, heat to dissolve, and dilute with water to 1 L.
- 7.10.3. Nitric acid (7M): Add 443 mL of concentrated HNO₃ to 400 mL of water and dilute with water to 1 L.
- 7.10.4. Nitric acid (8M): Add 506 mL of concentrated HNO₃ to 400 mL of water and dilute with water to 1 L.
- 7.11. Sodium carbonate (2M): Dissolve 212 g anhydrous Na₂CO₃ in 800 mL of water, then dilute with water to 1 L.
- 7.12. Sodium hydroxide pellets.
- 7.13. Titanium (III) chloride solution (TiCl₃), 20 percent by mass (wt%) solution in 20–30 wt% hydrochloric acid. (This reagent is typically available commercially in this concentration.) Alternate concentrations (e.g. 10%) may be used with appropriate volume adjustments.
- 7.14. Radioactive tracers/carriers (used as yield monitors) and spiking solutions. A radiotracer is a radioactive isotope of the analyte that is added to the sample to measure any losses of the analyte. A carrier is a stable isotope form of a radionuclide (usually the analyte) added to increase the total amount of that element so that a measureable mass of the element is present. A carrier can be used to determine the yield of the chemical process and/or to carry the analyte or radiotracer through the chemical process. Refer to the chemical separation method(s) to be employed upon completion of this dissolution technique. Tracers/carriers that are used to monitor radiochemical/chemical yield should be added at the beginning of this procedure. This allows for monitoring and correction of chemical losses in the combined digestion process, as well as in the chemical separation method. Carriers used to prepare sample test sources but not used for chemical yield determination (e.g., cerium (Ce) added for microprecipitation of plutonium or uranium), should be added where indicated.

8. Sample Collection, Preservation, and Storage

Not Applicable.

9. Quality Control

- 9.1. Where the subsequent chemical separation technique requires the addition of carriers and radioactive tracers for chemical yield determinations, these are to be added prior to beginning the fusion procedure, unless there is good technical justification for doing otherwise.
- 9.2. Quality control samples are generally specified in the laboratory's quality manual or in a project's analytical protocol specifications (APS). At the very minimum, the following are suggested:
- 9.2.1. A LCS, which consists solely of the reagents used in this procedure and a known quantity of radionuclide spiking solution, shall be run with each batch

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of samples. The concentration of the LCS should be at or near the action level or level of interest for the project.

- 9.2.2. One reagent blank shall be run with each batch of samples. The blank should consist solely of the reagents used in this procedure (including tracer or carrier noted in this analytical method added prior to the fusion process).
- 9.2.3. A sample duplicate that is equal in size to the original aliquant should be analyzed with each batch of samples. This provides assurance that the laboratory's sample size reduction and subsampling processes are reproducible.
- 9.3. Batch quality control results shall be evaluated and meet applicable APS prior to release of unqualified data. In the absence of project-defined APS or a project-specific quality assurance project plan (QAPP), the quality control sample acceptance criteria defined in the laboratory's Quality Manual and procedures shall be used to determine acceptable performance for this method.

10. Calibration and Standardization.

- 10.1. Refer to the individual chemical separation and analysis methods for calibration and standardization protocols.

11. Procedure

11.1. Fusion

- 11.1.1. In accordance with the data quality objectives (DQOs) and sample processing requirements stated in the project plan documents, remove extraneous materials from the limestone sample using a clean forceps or tweezers.
- 11.1.2. Weigh out a representative, finely milled 1-g aliquant of sample into a 250-mL crucible (0.75 g aliquants for ^{226}Ra analysis or 1.25 to 1.5 g aliquants for ^{90}Sr analysis). See Appendix A for the limestone milling procedure.

NOTE: For all analyses, a reagent blank of ~200-mg Ca per sample (prepared by evaporating 4 mL of 1.25M calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, should be added to the crucible as a blank simulant to ensure the blank behaves like the limestone samples during the precipitation steps.

- 11.1.3. Add the proper amount of tracer or carrier appropriate for the method being used and the number of aliquants needed.

NOTE: It is anticipated that limestone sample material will be dry enough to aliquant without a preliminary drying step. In the event samples are received that contain significant amounts of moisture, the samples may be dried in a drying oven at 105 °C prior to taking the aliquant.

- 11.1.4. Place crucibles on a hot plate and heat to dryness on medium heat.

NOTE: Heat on medium heat to dry quickly but not so high as to cause splattering.

- 11.1.5. Add the following amounts of sodium hydroxide (NaOH) based on the sample size/analysis required.

1 g for Pu, Am, U: 15 g NaOH

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1.25 g to 1.5 g for Sr: 15 g NaOH
0.75 g for Ra: 10 g NaOH

- 11.1.6. Place the crucibles with lids in the 600 °C furnace using tongs.
- 11.1.7. Fuse samples in the crucibles for ~15 minutes.
NOTE: Longer times may be needed for larger particles.
- 11.1.8. Remove hot crucibles from furnace very carefully using tongs, and transfer to hood.
- 11.1.9. Add ~25-50 mL of water to each crucible ~8 to 10 minutes (or longer) after removing crucibles from furnace, and heat on hotplate to loosen and dissolve solids.
- 11.1.10. If necessary for dissolution, add more water and warm as needed on a hotplate.
NOTE: If undissolved residues are visible after dissolving the fusion cake, the sample should be reprocessed using sample material that has been ground or milled to a finer particle size, or longer fusion times, or both.
- 11.1.11. Proceed to Section 11.2 for the actinide pre-concentration, 11.3 for strontium pre-concentration, or 11.4 for radium pre-concentration steps.

11.2. Pre-concentration of Actinides (Pu, U, or Am) from Hydroxide Matrix

NOTE: The iron (Fe) and La carriers may be added to the 225 mL centrifuge tubes prior to transferring the dissolved sample to the tubes.

- 11.2.1. After each fused sample has been transferred to a labeled 225-mL centrifuge tube, ensure crucibles have been rinsed well with water, and the rinses have been transferred to each tube.
- 11.2.2. Add 10 mL 3 M HNO₃ to each crucible and heat crucibles on a hot plate until hot. Transfer the 3M HNO₃ rinse to the 225 mL tube, followed by additional rinses of water.
- 11.2.3. Dilute each sample with water to ~160 mL.
- 11.2.4. Add 20 mL concentrated HCl to each tube and swirl to mix well.
Note: The hydroxide content is lowered to reduce the amount of Ca in the precipitate.
- 11.2.5. Cool the 225-mL centrifuge tubes in an ice bath to approximately room temperature.
- 11.2.6. Pipet 2.5 mL of iron carrier (50 mg/mL) into each 225-mL centrifuge tube for each sample.
- 11.2.7. Pipet 1 mg La/mL to each tube as follows:
Pu, U: 5-mL 1 mg La/mL
Am: 3-mL 1 mg La/mL
- 11.2.8. Pipet 4 mL 3.2M (NH₄)₂HPO₄ into each tube. Cap and mix well.

NOTE: If column load solution solids are encountered, it may be necessary to reduce the amount of phosphate added.

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- 11.2.9. Pipet 4 mL of 20 wt% titanium (III) chloride (TiCl_3) into each tube, and cap and mix well immediately.
- NOTE: Other strengths of TiCl_3 may be used, with the volume aliquot adjusted to add an equivalent amount of TiCl_3 , for example, 8 mL of 10% TiCl_3 . It is very important to mix well at this step to enhance uranium precipitation.**
- 11.2.10. Cool 225 mL centrifuge tubes in an ice bath for ~ 10 minutes.
- 11.2.11. Centrifuge tubes for ~6 minutes at 3500 rpm or more or as needed.
- 11.2.12. Pour off the supernate and discard to waste.
- 11.2.13. Add 1.5M HCl to each tube to redissolve each sample in a total volume of ~80 mL.
- 11.2.14. Cap and shake each tube to dissolve solids as well as possible.
- NOTE: Typically, there will be undissolved solids at this point, which is acceptable.**
- 11.2.15. Dilute each tube to ~170 mL with 0.01M HCl. Cap and mix.
- 11.2.16. Pipet 1 mL of 1.0 mg La/mL into each tube.
- 11.2.17. Pipet 2.5 mL of 20 wt% TiCl_3 into each tube. Cap and mix.
- 11.2.18. Add ~20 mL of concentrated HF into each tube. Cap and mix well.
- 11.2.19. Allow centrifuge tubes to stand for ~10 minutes.
- 11.2.20. Centrifuge for ~5 to 10 minutes at 3500 rpm or more or as needed.
- 11.2.21. Pour off supernate, and discard to waste.
- 11.2.22. Pipet 7 mL of 3M HNO_3 – 0.25M boric acid into each tube.
- 11.2.23. Cap, mix and transfer contents of the tube into a labeled 50-mL centrifuge tube.
- 11.2.24. Pipet 6 mL of 7M HNO_3 and 7 mL of 2M aluminum nitrate into each tube, cap and mix (shake or use a vortex stirrer), and transfer rinse to 50-mL centrifuge tubes.
- 11.2.25. Pipet 3 mL of 3M HNO_3 directly into the 50-mL centrifuge tube.
- 11.2.26. Warm each 50-mL centrifuge tube in a hot water bath for a few minutes, shaking or using a vortex mixer to dissolve.
- 11.2.27. If the sample does not clear up or appears cloudy, add 5 mL of 3M HNO_3 to the tube and mix again.
- 11.2.28. Remove each 50-mL centrifuge tube from the water bath and allow to cool to room temperature
- 11.2.29. Centrifuge the 50-mL centrifuge tubes at 3500 rpm for 5 minutes to remove any traces of solids (may not be visible prior to centrifuging), and transfer solutions to labeled beakers or tubes for further processing. Discard any solids.

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11.2.30. Proceed directly to the Am, Pu, or U methods listed in steps 1.1.1, 1.1.2, or 1.1.5.

11.3. Pre-concentration of ^{90}Sr from Hydroxide Matrix

NOTE: The Fe carrier may be added to the 225 mL centrifuge tubes prior to transferring the dissolved sample to the tubes.

- 11.3.1. After each fused sample has been transferred to a 225-mL centrifuge tube, ensure crucibles have been rinsed well with water, and the rinses have been transferred to each tube.
- 11.3.2. Add 10 mL 3 M HNO_3 to each crucible and heat crucibles on a hot plate until hot. Transfer the 3M HNO_3 rinse to the 225 mL tube, followed by additional rinses of water.
- 11.3.3. Dilute each sample to ~ 180 mL with water.
- 11.3.4. Cool the 225-mL centrifuge tubes in an ice bath to approximately room temperature.
- 11.3.5. Pipet 1 mL of iron carrier (50 mg/ mL) and 7 mL 3.2M $(\text{NH}_4)_2\text{HPO}_4$ into each tube.
- 11.3.6. Cap tubes and mix well
- 11.3.7. Cool 225 mL centrifuge tubes in an ice bath for 5 to 10 minutes.
- 11.3.8. Centrifuge tubes for ~6 minutes at 3500 rpm or more or as needed.
- 11.3.9. Pour off the supernate and discard to waste.
- 11.3.10. Add 1.5M HCl to each tube to redissolve each sample in a total volume of ~80 mL.
- 11.3.11. Cap and shake each tube to dissolve solids as well as possible.
NOTE: Typically, there will be undissolved solids, which is acceptable.
- 11.3.12. Dilute each tube to ~170 mL with 0.01M HCl. Cap and mix.
- 11.3.13. Add ~15 mL of concentrated HF into each tube. Cap and mix well.
- 11.3.14. Allow tubes to sit for 5 to 10 minutes.
- 11.3.15. Centrifuge for ~6 minutes at 3500 rpm or more or as needed.
- 11.3.16. Pour off supernate and discard to waste.
- 11.3.17. Pipet 7 mL of concentrated HNO_3 and 7 mL of 3M HNO_3 - 0.25M boric acid into each 225-mL centrifuge tube to dissolve precipitate.
- 11.3.18. Cap and mix well. Transfer contents of the tube into a labeled 50-mL centrifuge tube.
- 11.3.19. Pipet 7 mL of 3M HNO_3 and 7 mL of 2M aluminum nitrate into each 225 mL tube, cap tube and mix.
- 11.3.20. Transfer rinse solutions to 50-mL centrifuge tubes and mix well (shake or use vortex stirrer).

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- 11.3.21. Centrifuge the 50-mL tubes at 3500 rpm for 5 minutes to remove any traces of solids.
 - 11.3.22. Transfer solutions to labeled beakers or new 50-mL centrifuge tubes for further processing.
 - 11.3.23. If solids remain, add 5 mL 3M HNO₃ to each tube, cap and mix well, centrifuge for 5 minutes and add the supernate to the sample solution. Discard any residual solids.
 - 11.3.24. Proceed directly to the Sr method listed in step 1.1.4
- 11.4. Pre-concentration of ²²⁶Ra from Hydroxide Matrix
- 11.4.1. Transfer each sample to a 225-mL centrifuge tube, rinse crucibles well with water, and transfer rinses to each tube.
 - 11.4.2. Dilute to ~ 150 mL with water.
 - 11.4.3. Add 10 mL concentrated HCl to each tube.
 - 11.4.4. Cap and mix each tube well.
 - 11.4.5. Add 10 mL of 2M Na₂CO₃ to each tube.
 - 11.4.6. Cap tubes and mix.
 - 11.4.7. Allow centrifuge tubes to stand for 10 minutes.
 - 11.4.8. Centrifuge tubes for 6 minutes at 3500 rpm.
 - 11.4.9. Pour off the supernate and discard to waste.
 - 11.4.10. Pipet 10 mL of 1.5M HCl into each tube to dissolve precipitate. Cap and mix.
 - 11.4.11. Transfer sample solution to a 50-mL centrifuge tube.
 - 11.4.12. Pipet 10 mL of 1.5M HCl into each 225-mL centrifuge tube to rinse. Cap and rinse well.
 - 11.4.13. Transfer rinse solution to 50-mL tube and mix well using shaking or vortex stirrer.

Note: Typically, the HCl added to dissolve the carbonate precipitate is sufficient to acidify the sample. If the precipitate was unusually large and suspended solids remain, additional acid may be needed. The pH can be checked to verify it is pH 1 or less. To acidify the pH <1, add 1 or 2 mL of concentrated hydrochloric acid to the solution and get it to clear. Tubes may be warmed in a water bath or hot block to help dissolve samples.
 - 11.4.14. If solids remain, add 5-mL 1.5M HCl to each tube, cap and mix well, centrifuge for 5 minutes and add the supernate to the sample solution. Discard any residual solids.
 - 11.4.15. Proceed directly to the Ra method listed in step 1.1.3
 - 11.4.16. The following steps in the Ra-226 specific method listed in step 1.1.3 need to be modified slightly to handle the very high Ca levels in limestone samples (Section 11.2):
 - 11.4.16.1. Add a water slurry (or weigh out the solid resin) of cation resin 50WX8 (200-400 mesh) into each column equivalent to 8 g of resin.

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11.4.16.2. Add 50 mL of 3M HCl to each column at ~1-2 mL/min. Discard rinse.

12. Data Analysis and Calculations

- 12.1. Equations for determination of final result, combined standard uncertainty, and radiochemical yield (if required) are found in the corresponding chemical separation and analysis methods, with the units being provided by the project manager.
- 12.2. In cases where samples have elevated activity, smaller initial sample aliquants may be taken from the original sample. Alternately, smaller aliquant volumes may be taken from the final sample volume containing the dissolved precipitate (digestate). Aliquants should be removed carefully and accurately from this final sample volume.

NOTE: Small aliquants taken from the final sample digestate for Sr and Ra analysis may be used in the respective analytical procedures as is. Smaller aliquants for actinide analysis should be diluted to a 15-mL total volume with 3M HNO₃ so that load solution acidity is maintained when valence adjustment reagents are added.

For a single split, the effective size of sample is calculated:

$$W_a = W_s \frac{D_a}{D_s} \quad (\text{Equation 1})$$

Where:

- W_s = original sample size, in the units designated by the project manager (e.g., kg, g, etc.)
- D_s = mass or volume of the entire final digestate, (e.g., 20 mL, etc.).
- D_a = mass or volume of the aliquant of digestate used for the individual analyses, (e.g., 5.0 mL, etc.). Note that the values for D_a must be in the same units used in D_s .
- W_a = sample aliquant size, used for analysis, in the units designated by the project manager (e.g., kg, g, etc.).

NOTE: For higher activity samples, additional dilution may be needed. In such cases, Equation 1 should be modified to reflect the number of splits and dilutions performed. It is also important to measure the masses or volumes, used for aliquanting or dilution, to enough significant figures so that their uncertainties have an insignificant impact on the final uncertainty budget. In cases where the sample will not be split prior to analysis, the sample aliquant size is simply equal to the original sample size, in the same units requested by the project manager.

13. Method Performance

- 13.1. Method validation results are to be reported.
- 13.2. Expected turnaround time per sample
 - 13.2.1. For a representative, finely ground 1-g aliquant of sample, the fusion steps should add approximately 1 hour per batch to the time specified in the individual chemical separation methods.
 - 13.2.2. The pre-concentration steps should add approximately 1 to 1.5 hours per batch.

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NOTE: Processing times for the subsequent chemical separation methods are given in those methods for batch preparations.

14. Pollution Prevention

This method inherently produces no significant pollutants. The sample and fusion reagents are retained in the final product and are carried into the ensuing chemical separation techniques, which marginally increases the salt content of the effluent waste. It is noted that if the sampled particulates include radionuclides that may be volatile under the fusion conditions, these constituents will be exhausted through the fume hood system.

15. Waste Management

15.1. Refer to the appropriate chemical separation methods for waste disposal information.

16. References

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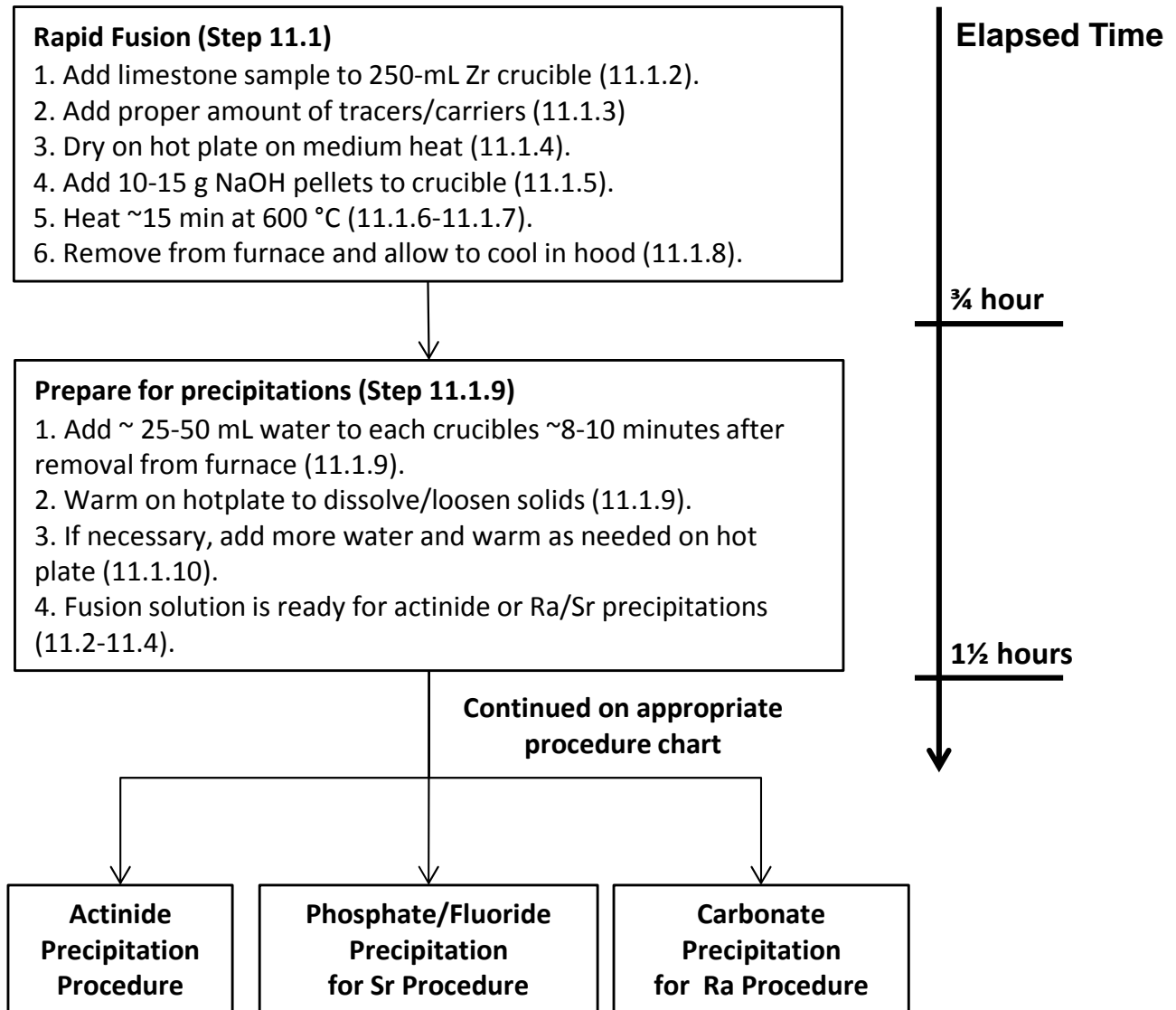
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17. Tables, Diagrams, and Flow Chart

Note: The following flowcharts and timelines address processes as they apply specifically to limestone matrices as described in this method. The approach and timeline may deviate from information provided in Section 17 of the corresponding Building Materials Methods (references 16.1 – 16.5).

17.1. Fusion Flow Chart

Rapid Fusion and Preparation of Limestone Samples for Precipitation and Analysis



17.2. Actinide Precipitation Flow Chart

Actinide Precipitation Procedure

Continued from 17.1 Fusion Flow Chart

1. Add Fe and La to each tube (11.2.1-11.2.2).
2. Add 10 mL 3M HNO₃ and heat until hot. Transfer to 225-mL tube (11.2.4)
3. Dilute to ~160 mL with water (11.2.5).
4. Add 20 mL concentrated HCl to each tube and swirl to mix (11.2.6).
5. Cool to room temperature in ice bath (11.2.7).
6. Add 4 mL 3.2M (NH₄)₂HPO₄ to each tube. Cap and mix (11.2.8).
7. Add 4 mL 20 wt% TiCl₃ to each tube. Cap and mix (11.2.9).
8. Cool in ice bath for ~10 min (11.2.10).
9. Centrifuge for 6 min and pour off supernate (11.2.11-11.2.12).
10. Redissolve in 1.5M HCl to total volume of ~80mL Cap and shake. (11.2.13-11.2.14).
11. Dilute to ~170 mL with 0.01M HCl. Add La (11.2.15-11.2.16).
12. Add 2.5 mL 20 wt% TiCl₃, ~10mL HF and allow to stand for 10min (11.2.16-11.2.19).
13. Centrifuge for 5-10 min and pour off supernate (11.2.20-11.2.21).
14. Redissolve in 7 mL 3M HNO₃-0.25M H₃BO₃ + 6 mL 7M HNO₃ + 7 mL 2M Al(NO₃)₃ + 3 mL 3M HNO₃, warming to dissolve in 50-mL centrifuge tubes (11.2.22-11.2.26).
15. If samples do not clear up, add 5mL 3M HNO₃ and mix again (11.2.27).
16. Remove from water bath and allow to cool to room temperature. Centrifuge to remove trace solids and transfer to beakers or tubes for processing (11.2.28-11.2.29).
17. Analyze sample solutions for specific actinides using rapid methods for specific actinides in building materials (11.2.30).

Elapsed Time

1½ hours

3 hours

17.3. Strontium Precipitation Flow Chart

Ca₃(PO₄)₂ / CaF₂ Precipitation Procedure for Sr

Continued from Fusion Flow Chart Step 17.1

1. Add 10 mL 3 M HNO₃ and heat until hot. Transfer to 225-mL tube (11.3.2)
2. Dilute to ~180 mL with water (11.3.3).
3. Cool tubes to room temperature in ice bath (11.3.4).
4. Pipet 1 mL 50 mg/mL iron carrier, and 7 mL 3.2M (NH₄)₂HPO₄ to each tube. Cap and mix well (11.3.5-11.3.6).
5. Cool tubes to 5 to 10 min in ice bath (11.3.7).
6. Centrifuge for 6 min and pour off supernate (11.3.8-11.3.9).
7. Redissolve in ~80 mL 1.5M HCl. Cap and mix well. (11.3.10-11.3.11).
8. Dilute to ~170 mL with 0.01M HCl (11.3.12).
9. Add 20 mL concentrated HF and wait 5-10 min (11.3.13-11.3.14).
10. Centrifuge for ~6 min and pour off supernate (11.3.15-11.3.16).
11. Redissolve in 7 mL 3M HNO₃-0.25M H₃BO₃ + 7 mL concentrated HNO₃ +7 mL 2M Al(NO₃)₃ + 7 mL 3M HNO₃. Transfer to 50-mL tube (11.3.17-11.3.20).
12. Cap and mix using vortex stirrer or by shaking (11.3.20).
13. Centrifuge for 5 min and discard trace solids. Transfer solutions to new tubes or beakers. (11.3.21-11.3.22).
14. Analyze sample solutions for ⁹⁰Sr using ⁹⁰Sr method for building materials. (11.3.24)

Elapsed Time

1½ hours

2½ hours

17.4. Radium Precipitation Flow Chart

Carbonate Precipitation for Radium Procedure

Continued from Fusion Flow Chart Step 17.1

1. Dilute to 150 mL with water. Add 10 mL concentrated HCl. Cap and mix (11.4.2-11.4.4).
2. Add 10 mL 2M Na₂CO₃ to each tube. Cap and mix (11.4.5-11.4.6).
3. Allow to stand 10 min (11.4.7).
4. Centrifuge for 6 min and pour off supernate (11.4.8-11.4.9).
5. Redissolve in 10 mL 1.5 M HCl (11.4.10).
6. Transfer to 50-mL centrifuge tubes (11.4.11).
7. Rinse 225-mL tube with 10 mL 1.5M HCl and transfer to 50-mL tube. Cap and mix using vortex stirrer or by shaking (11.4.12-11.4.13).
8. If solids remain, add 5 mL 1.5M HCL, cap and mix. Centrifuge for 5 min and discard trace solids (11.4.14).
9. Analyze sample solutions for ²²⁶Ra using ²²⁶Ra method for building materials (11.4.15)

Elapsed Time

1½ hours

3 hours

Appendix A:

Rapid Technique for Milling and Homogenizing Limestone Samples

A1. Scope and Application

- A1.1. Limestone samples may be received as core samples, chunks or crushed pieces. The goal is to obtain representative sample aliquants from homogeneous amounts of sample. Significant effort should be applied to ensure representative sampling of the limestone materials.
- A1.2. This method describes one approach for the rapid, gross preparation of limestone samples to yield representative 0.75–1.5 g aliquant for radiochemical analysis of non-volatile radionuclides. The method addresses steps for splitting, and milling of 50–1000-g limestone samples. The limestone sample must be reduced to pieces or fragments less than ~25 mm in diameter prior to using the ball mill. This can be done with a hydraulic press or mallet. A mortar grinder may be needed to reduce the particle size if a mallet or hammer will not crush the particles to a fine enough size.
- A1.3. The method is designed to be used as a preparatory step for the attached methods for furnace heating and fusion of limestone for measurement of ^{241}Am , ^{238}Pu , $^{239/240}\text{Pu}$, U, ^{90}Sr , and ^{226}Ra . It may also be applied to other matrices whose physical form is amenable to pulverization.
- A1.4. If the levels of activity in the sample are low enough to permit safe radiological operations, up to 1 kg of limestone can be processed.

A2. Summary of Methods

- A2.1. This method uses disposable equipment or materials to contact the sample, minimizing the risk of contamination and cross-contamination and eliminating concerns about adequate cleaning of equipment.
- A2.2. The entire sample as received (after reducing fragment size to less than ~25 mm diameter) is split by coning and quartering until ~75-150 mL of the limestone is available for subsequent processing. If less than ~450 mL of limestone is received, the entire sample is processed without splitting.
NOTE: Large chunks of limestone will require initial crushing prior to coning and quartering.
- A2.3. The limestone is transferred to a hydraulic press and crushed. A ball mill approach with disposable paint cans (or equivalent) is used to mill the samples into fine particles.
- A2.4. Other milling apparatus, such as lab pulverizers/crushers, also may be used to mill the limestone sample to finely ground, well-homogenized, particles. In this case, effort must be made to ensure no sample carry-over effects occur between the processing of individual samples.
- A2.5. Additional replicate analyses may also be performed to provide further assurance that analytical results are representative of limestone samples received.

A3. Definitions, Abbreviations, and Acronyms

A3.1. Discrete Radioactive Particles (DRPs or “hot particles”). Particulate matter in a sample of any matrix where a high concentration of radioactive material is contained in a tiny particle (μm range).

A3.2. *Multi-Agency Radiological Analytical Laboratory Protocols (MARLAP) Manual* (Reference A16.1).

A4. Interferences

A4.1. Radiological Interferences

A4.1.1. Coning and quartering provides a mechanism for rapidly decreasing the overall size of the sample that must be processed while optimizing the representativeness of the subsampling process. By decreasing the time and effort needed to prepare the sample for subsequent processing, sample throughput can be significantly improved.

A4.1.2. Openly handling large amounts of highly contaminated materials, however, even within the containment provided by a fume hood, may pose an unacceptable risk of inhalation of airborne contamination and exposure to laboratory personnel from radioactive or other hazardous materials. Similarly, it may unacceptably increase the risk of contamination of the laboratory. In such cases, coning and quartering process may be eliminated in lieu of processing the entire sample.

A4.1.3. The precise particle size of the milled sample is not critical to subsequent processes. However, milling the sample to smaller particle sizes, and thorough mixing, both facilitate representative subsampling by minimizing the amount of sample that is not pulverized to fine mesh and must be discarded. Additionally, subsequent fusion and digestion processes are more effective when performed on more finely milled samples.

A4.1.4. This method assumes that radioactivity in the sample is primarily adsorbed onto the surface of particles, as opposed to being present as a hot particle (see discussion of DRPs below). Thus, nearly all of the activity in a sample will be associated with sample fines. By visually comparing the sample to a qualitative standard of ~50–100 mesh size particles, it is possible to rapidly determine whether the sample is fine enough to facilitate the subsequent fusion or digestion. This method assumes that when greater than 95% of the sample is as fine or finer than the 50–100 mesh standard, bias imparted from losses of larger particles will be minimal.

A4.1.5. If the sample was collected near the epicenter of a radiological dispersal device (RDD) or improvised nuclear device (IND) explosion, it may contain millimeter (mm)- to micrometer (μm)-sized particles of contaminant referred to as DRPs. DRPs may consist of small pieces of the original radioactive source and thus may have very high specific activity. They may also consist of chemically intractable material and present

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special challenges in the analytical process. Even when the size is reduced to less than 50–100 mesh, these particles may resist fusion or digestion of the solids into ionic form that can be subjected to chemical separations.

- A4.1.6. When DRPs are present, this method isolates larger particles by passing the sample through a disposable 50-mesh screen after which they can be reliably checked for radioactivity. DRPs may reliably be identified by their very high specific activity which is readily detectable since they show high count rates using hand-held survey equipment such as a thin-window Geiger-Muller (G-M) probe.
- A4.1.7. When present, DRPs may be further milled and then recombined with the original sample. Alternatively, the particles, or the entire sample may need to be processed using a different method capable of completely solubilizing the contaminants such that the radionuclides they contain are available for subsequent chemical separation.

A5. Safety

A5.1. General

- A5.1.1. Refer to your laboratory's safety manual for concerns of contamination control, personal exposure monitoring, and radiation dose monitoring.
- A5.1.2. Refer to your laboratory's chemical hygiene plan (or equivalent) for general safety rules regarding chemicals in the workplace.

A5.2. Radiological

- A5.2.1. Refer to your radiation safety manual for direction on working with known or suspected radioactive materials.
- A5.2.2. This method has the potential to generate airborne radioactive contamination. The process should be carefully evaluated to ensure that airborne contamination is maintained at acceptable levels. This should take into account the activity level, and physical and chemical form of contaminants possibly present, as well as other engineering and administrative controls available.
- A5.2.3. Discrete Radioactive Particles (DRPs or hot particles)
 - A5.2.3.1. Hot particles will usually be small, on the order of 1 mm or less. Typically, DRPs are not evenly distributed in the media, and their radiation emissions are not uniform in all directions (anisotropic).

A5.3. Method-Specific Non-Radiological Hazards

- A5.3.1. This method employs a hydraulic press and/or paint can shaker should. The method and equipment should be evaluated for personnel hazards associated with the crushing process.

A6. Equipment and supplies

- A6.1. Aluminum foil loaf pans, disposable.

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- A6.2. Balance, top-loading, range to accommodate sample size encountered, readability to $\pm 1\%$.
- A6.3. Butcher paper or equivalent.
- A6.4. Drying oven, at 110 ± 10 °C.
- A6.5. Disposable wire cloth – nominal 48 mesh size (~ 300 μm).
- A6.6. Disposable sieves, U.S. Series No. 50 (300 μm or 48 mesh) and U.S. Series No. 100 (150 μm or 100 mesh).
- A6.7. Hydraulic press.
- A6.8. Disposable scoop, scraper, tongue depressor or equivalent.
- A6.9. Red Devil 5400 mechanical paint shaker or equivalent.
- A6.10. Steel paint cans and lids (pint, quart, 2 quart, 1 gallon, as needed).
- A6.11. Steel or ceramic grinding balls or rods for ball milling, ~ 15 – 25 -mm diameter. The size and number of grinding media used should be optimized to suit the types of limestone pieces, the size of the can, and the volume of limestone processed.
- A6.12. Mallet or hammer.
- A7. Reagents and Standards
No reagents needed.
- A8. Sample Collection, Preservation and Storage
 - A8.1. Samples should be collected in appropriately sized plastic, metal or glass containers.
 - A8.2. Solid sample volumes equivalent to approximately 500 mL of sample will require two splits to obtain a ~ 100 mL sample.
- A9. Quality Control
 - A9.1. Batch quality control results shall be evaluated and meet applicable analytical protocol specifications (APSs) prior to release of unqualified data. In the absence of project-defined APS or a project-specific quality assurance project plan (QAPP), the quality control sample acceptance criteria defined in the laboratory quality manual and procedures shall be used to determine acceptable performance for this method.
 - A9.2. Quality control samples should be initiated as early in the process as possible. Since the risk of cross-contamination using this process is relatively low, initiating blanks and laboratory control samples at the start of the chemical separation process is acceptable. If sufficient sample is available, a duplicate sample should be prepared from the two discarded quarters of the final split of the coning and quartering procedure.
- A10. Procedure

NOTE: This method ensures that only disposable equipment or materials come in contact with sample materials to minimize the risk of sample cross-contamination and concerns about adequate cleaning of

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equipment. Under certain circumstances, such as disposable equipment not being available; careful, thorough cleaning of the equipment with water and then ethanol may be an option.

A10.1. Estimate the total volume of sample, as received.

NOTE: Limestone samples typically do not contain large amounts of moisture. Large chunks of limestone will require crushing prior to coning and quartering. The next step uses absorbent paper in the reverse fashion from the normal use of this type of paper; it allows for a smooth division of the sample and control of contamination.

A10.1.1. Spread a large piece of plastic in a hood (or alternate paper material which can be discarded to waste later).

A10.1.2. If the limestone sample is received with chunks that are too large to cone and quarter, crush the larger pieces to manageable size using a hydraulic press.

A10.1.2.1. Wrap limestone pieces in butcher paper and place in small disposable aluminum foil pan. Place another aluminum foil pan on top of wrapped limestone sample.

A10.1.2.2. Crush sample between the aluminum foil pans using a hydraulic press.

A10.1.2.3. Break crushed pieces into smaller pieces for coning and quartering. A hammer or mallet can be used to crush further, if needed.

A10.1.2.4. Unwrap crushed limestone and break apart into smaller pieces for coning and quartering, then ball milling. A mortar grinder may be needed to reduce the size of hard limestone rock particles further.

A10.1.3. If the sample volume is less than ~450 mL, there is no benefit to coning and quartering (Reference A16.1).

A10.1.3.1. Carefully pour the sample onto the paper.

A10.1.4. If the sample volume is greater than ~450 mL, carefully pour the entire sample into a cone onto the paper.

A10.1.5. The sample is split at least twice using the coning and quartering steps that follow.

NOTE: Unused quarters are considered representative of the original sample and may be reserved for additional testing.

A10.1.5.1. Spread the material into a flat circular cake of limestone using a tongue depressor or other suitable disposable implement. Divide the cake radially and return two opposing quarters to the original sample container.

A10.1.5.2. Reshape the remaining two quarters into a smaller cone, and repeat Step A10.1.5.1 until the total volume of the remaining material is approximately 100–150 mL.

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A10.1.6. Transfer the coned and quartered limestone sample to a tared, labeled 1-pint paint can. If the initial total volume (Step A10.1.3) was less than ~450 mL, transfer the entire sample to a tared, labeled 1-quart paint can.

A10.2. Place the can (without lid) in an oven at 110 ± 10 °C and dry the limestone to constant mass.

NOTE: Limestone samples may be dry enough such that heating prior to homogenizing the sample is not required.

A10.3. Weigh the combined mass of the can, sample, and lid. If the percent solids are required see Section A12.1 calculations. Remove can from oven. Allow to cool.

A10.4. Add two to five 1.5–2.5-centimeter (cm) stainless-steel or ceramic balls to the can. Replace the lid and seal well.

A10.5. Shake the can and contents for 5 minutes, or longer, as needed to produce a finely-milled, well-homogenized, sample.

NOTE: Although the precise particle size of the milled sample is not critical, complete pulverization and fine particle size facilitates representative subsampling and subsequent fusion or digestion processes. A qualitative standard can be prepared by passing quartz sand or other milled material through a 50-mesh and then a 100-mesh screen. The portion of the sample retained in the 100 mesh screen can be used as a qualitative visual standard to determine if samples have been adequately pulverized.

A10.6. Visually compare the resulting milled sample to a qualitative 50–100 mesh pulverized sample (~150–300 μm or 50–100 mesh using the Tyler screen scale). The process is complete once 95% of the sample (or greater) is as fine, or finer, than the qualitative standard. If, by visual estimation, more than ~5% of total volume of the particles in the sample appear to be larger than the particle size in the standard, return the sample to the shaker and continue milling until the process is complete.

A10.7. Following milling, a small fraction of residual larger particles may remain in the sample.

NOTE: The following steps offer guidance that may be used if larger-particle DRPs are encountered. The goal is to crush and mill and homogenize the limestone samples in a way that allows representative aliquants to be taken for analysis. This guidance may be modified as needed by the incident commander.

A10.7.1. If the sample was collected close to the epicenter of an RDD or IND explosion, it may also contain particles of contaminant referred to as DRPs. In such a case, the larger particles should be isolated by passing through a disposable 50 mesh screen and checked for radioactivity. DRPs are readily identified by their very high specific activity which is detectable using hand-held survey equipment such as a thin-window G-M probe held within an inch of the particles.

A10.7.1.1. If radioactivity is clearly detected, the sieved material is returned to the can and ball milled until the desired mesh is obtained. In some cases, these materials may be resistant to

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further pulverization and may need to be processed according to a method specially designed to address highly intractable solids.

A10.7.1.2. If the presence of DRPs is of no concern (no high activities detected for specific particles), the larger particles need not be included in subsequent subsamples taken for analysis. It may be possible to easily avoid including them during aliquanting with a disposable scoop. If not, however, they should be removed by sieving through a nominal 50 mesh screen (disposable) prior to further subsampling for subsequent analyses.

A10.8. Sample fines may be stored in, and aliquanted directly from, the container used for pulverization, if the paint can ball mill approach was used.

A11. Calibration and Standardization

A11.1. Balances used shall be calibrated using National Institute of Standards and Technology (NIST)-traceable weights according to the process defined by the laboratory's quality manual.

A12. Data Analysis and Calculations

NOTE: Limestone samples may be dry enough such that heating prior to homogenizing the sample is not required. Heating to a constant mass may be difficult due to the presence of volatile organics.

A12.1. The percent solids (dry-to-as-received mass ratio) for each sample is calculated from data obtained during the preparation of the sample as follows:

$$\% \text{ Solids} = \frac{M_{\text{dry}} - M_{\text{tare}}}{M_{\text{as rec}} - M_{\text{tare}}} \times 100$$

Where:

$$\begin{aligned} M_{\text{dry}} &= \text{mass of dry sample} + \text{labeled can} + \text{lid (g)} \\ M_{\text{tare}} &= \text{tare mass of labeled can} + \text{lid (g)} \\ M_{\text{as rec,}} &= \text{mass of sample as received} + \text{labeled can} + \text{lid (g)} \end{aligned}$$

A12.2. If requested, convert the equivalent mass of sample, as received, to dry mass. Dry mass is calculated from a measurement of the total as received mass of the sample received as follows:

$$\text{Dry Sample Equivalent} = M_{\text{total-as rec.}} \times \frac{\% \text{ Solids}}{100}$$

Where:

$$M_{\text{total-as rec.}} = \text{total mass of sample, as received (g)}$$

A12.3. Results Reporting

A12.3.1. The result for percent solids and the approximate total mass of sample as received should be reported for each result.

A13. Method Performance

Sodium Hydroxide Fusion of Limestone Matrices

A13.1. Results of method validation performance are to be archived and available for reporting purposes.

A13.2. Expected turnaround time for these sample preparation steps is about 3 hours for an individual sample and about 4 hours per batch.

A14. Pollution Prevention.

Not applicable

A15. Waste Management

A15.1. All radioactive and other regulated wastes shall be handled according to prevailing regulations.

A16. References

A16.1. EPA 2004. *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (MARLAP). EPA 402-B-1304 04-001A, July. Volume I, Chapters 6, 7, 20, Glossary; Volume II and Volume III, Appendix G. Available at <http://www2.epa.gov/radiation/multi-agency-radiological-laboratory-analytical-protocols-manual-marlap>.

A16.2. International Union of Pure and Applied Chemistry (IUPAC). 1997. *Compendium of Chemical Terminology*, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford. XML on-line corrected version: <http://goldbook.iupac.org/C01265.html>. (2006) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. Last update: 2010-12-22.